ON THE ACTION OF SODIC ETHYLATE ON TRIBROMDINITROBENZOL.

By C. Loring Jackson and Waldemar Koch.

THE principal object of the work described in this paper was to determine the constitution of the dinitroresorcine diethylether melting at 133°, formed by the action of a hot solution of sodic ethylate on tribromdinitrobenzol ($Br_3$1,3,5$(NO_2)_2$2,4), or on the bromdinitroresorcine diethylether melting at 184°. This determination was of interest to us, as it formed part of an investigation of the replacement of bromine by hydrogen under the influence of sodium malonic ester, sodic ethylate, and similar reagents, which has now been in progress for several years in this Laboratory. In all the cases studied here, with a single exception, the atom of bromine (or iodine) has stood between two other radicals, each in the ortho position to it, and it was necessary to determine whether this arrangement also existed in this case, since a consideration of the possibilities shows that this dinitroresorcine diethylether might have either the symmetrical structure, if the bromine between the two nitro groups was replaced by hydrogen, or the adjacent structure, if this replacement occurred with one of the other atoms of bromine.

The constitution of the diethylether was determined by saponifying it to the corresponding dinitroresorcine, which proved to be the symmetrical compound $(OH)_2$1,5$(NO_2)_2$2,4, melting at 212°.5, according to Typke.* The proof that this body has the structure assigned to it has been given by Nietzki and Schmidt,† who converted it into diimidoresorcine, which in turn yielded dioxyquinone by treatment with sodic hydrate, and this dioxyquinone gave with nitric acid nitranilic acid, which is paradinitro-dioxyquinone, a result that is in harmony only with the symmetrical structure for the dinitroresorcine. It follows therefore that the bromine replaced by hydrogen in tribromdinitrobenzol is the one between the

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* Ber. d. chem. Ges., XVI. 552.   † Ibid., XXI. 2374.

two nitro groups, as we had expected from the results of previous experiments, and that the bromdinitroresorcine diethylether melting at 184° has the constitution $(OC_2H_5)_2 1,5,Br3.(NO_2)_2 2,4$. It is an interesting fact in this connection that an isomeric bromdinitroresorcine diethylether (having the constitution $(OC_2H_5)_2 1,3,Br5,(NO_2)_2 2,4)$, in which the bromine is not in the ortho position to two nitro groups, gave no replacement of the atom of bromine by hydrogen, but, when treated with sodic ethylate, gave dinitrophloroglucine triethylether by the replacement of the bromine by an ethoxy group. Beilstein, in the third edition of his Handbuch, provisionally places the diethylether $C_6H_2(OC_2H_5)_2(NO_2)_2$ melting at 133°, and the corresponding dimethylether $C_6H_2(OCH_3)_2(NO_2)_2$ melting at 167°, prepared from tribromdinitrobenzol by W. H. Warren and one of us,[*] under the adjacent dinitroresorcine. The determination of the constitution of the diethylether just given necessitates their transfer to the symmetrical dinitroresorcine, as there can be no question that the methylether has the same structure as the ethyl compound. It also shows that the dimethylether $C_6H_2(OCH_3)_2(NO_2)_2$ melting at 67°, prepared by Hönig[†] by the direct action of nitric acid on a solution of resorcine dimethylether in glacial acetic acid, cannot have the symmetrical structure which Beilstein assigned to it, as this now belongs to the body melting at 167°.

In addition to this determination of the constitution of dinitroresorcine diethylether, we have made a more careful study of the products of the reaction between sodic ethylate and tribromdinitrobenzol melting at 192° both at ordinary temperatures and when aided by heat. These reactions had been already studied by W. H. Warren and one of us,[‡] with the result that in the cold the bromdinitroresorcine diethylether melting at 184° was formed, whereas, when hot, the dinitroresorcine diethylether melting at 133° was the product isolated. As, however, subsequent work[§] upon the tribromtrinitrobenzol showed that in that case the action was far from simple, it hardly seemed probable that the dinitro compound had given only one organic product in each of these cases, and this inference was confirmed by our first new experiment in this field, as we found sodic nitrite as well as sodic bromide among the products of the reaction, so that it was evident that some other compounds were present besides those recognized by Warren and one of us. The result of this later work was

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[*] These Proceedings, XXV. 170, 178.
[†] Ber. d. chem. Ges., XI. 1041.
[‡] These Proceedings, XXV. 166.
[§] Jackson and Warren, Ibid., XXVII. 283.

the isolation of the following products of the action of sodic ethylate on tribromdinitrobenzol, melting point 192°, when absolute alcohol and benzol are used as the solvents, and the mixture is allowed to stand at ordinary temperatures : —

(1) Bromdinitroresorcine diethylether $C_6HBr(OC_2H_5)_2(NO_2)_2$, melting at 184°, $(OC_2H_5)_21,5,Br3,(NO_2)_22,4$.

(2) Bromdinitroresorcine diethylether $C_6HBr(OC_2H_5)_2(NO_2)_2$, melting at 92°, $(OC_2H_5)_21,3,Br5,(NO_2)_22,4$.

(3) Tribromnitrophenol $C_6HBr_3(NO_2)OH$, melting at 90°, $Br_31,3,5$, $NO_22,OH4$.

(4) Dinitroresorcine monoethylether $C_6H_2(OC_2H_5)OH(NO_2)_2$, melting at 77°, $(OC_2H_5)1,OH5,NO_22,4$.

(5) Dinitrophloroglucine triethylether $C_6H(OC_2H_5)_3(NO_2)_2$, melting at 105°, $(OC_2H_5)_31,3,5,(NO_2)_22,4$.

These products indicate that there are three primary reactions, when sodic ethylate acts on tribromdinitrobenzol. These are, Reactions I. and II., consisting in the replacement of two atoms of bromine by two ethoxy groups, producing the two isomeric bromdinitroresorcine diethylethers (1) and (2), and Reaction III., in which one nitro group is replaced by one hydroxyl group (or by an ethoxy group followed by saponification) giving the tribromnitrophenol (3). There are also two secondary reactions owing to the further action of sodic ethylate on the products of Reactions I. and II.; first, the replacement of the bromine in the bromdinitroresorcine diethylether (1) by an atom of hydrogen (followed by partial saponification) giving the dinitroresorcine monoethylether (4); and secondly, the replacement of the bromine in the bromdinitroresorcine diethylether (2) by an ethoxy group giving the dinitrophloroglucine triethylether (5). The saponification mentioned in this paragraph might be brought about by the sodic hydrate formed from the sodic ethylate by the water added in the course of the purification, but it seems to us more probable that the phenols were formed by some sodic hydrate acting directly on the tribromdinitrobenzol, since the ethers of the phenols seemed decidedly stable, when treated with an alkali.

The following estimations of the approximate yields of the products give a rough idea of the extent to which each of the three primary reactions ran : —

Reaction I., forming substances (1) and (4) . . . 28 per cent.
Reaction II., forming substances (2) and (5) . . . 38 per cent.
Reaction III., forming substance (3) . . . . . . 1 per cent.

        Total . . . . 67 per cent.

As most of these substances were purified by crystallization, too much weight must not be given to these yields, but we can safely infer from them that Reaction II. ran to the largest extent, Reaction I. came next, and Reaction III. took place only to a very limited extent.

These results are capable of a satisfactory theoretical explanation, but before giving this it will be well to consider a parallel case studied by W. H. Warren and one of us,[*] in which the conditions are simpler and rather better marked. This is the action of sodic ethylate on symmetrical tribromtrinitrobenzol $C_6Br_3(NO_2)_3$, $Br_3 1,3,5,(NO_2)_3 2,4,6$, which consisted of two simultaneous reactions, first, the replacement of two nitro groups by two ethoxy groups, giving $C_6Br_3NO_2(OC_2H_5)_2$, and second, the replacement of the three bromine atoms by three ethoxy groups, giving $C_6(OC_2H_5)_3(NO_2)_3$. These two reactions ran to nearly an equal extent (about 45 per cent of each product), if the solvent was alcohol only.[†] In attempting to explain these experimental results we must consider the agencies which tend to loosen the nitro groups on the one hand and the atoms of bromine on the other from the benzol ring. We have designated these agencies by letters, and arranged them in the order of intensity, beginning with the strongest.

A. The loosening effect of the three nitro groups on the three atoms of bromine. This is a strong agency, as shown by the fact that picrylchloride (in which the chlorine is similarly disposed to the three nitro groups) is decomposed easily and completely, even at ordinary temperatures.[‡]

B. The loosening effect exerted by the three nitro groups on each other. Lobry de Bruyn [§] has shown that symmetrical trinitrobenzol is converted into dinitroanisol by sodic methylate, even at ordinary temperatures; this loosening effect is therefore a powerful one, but not quite so strong as *A*, since the action with picrylchloride is complete in a few minutes, whereas the reaction with trinitrobenzol needs several days, if carried on in the cold.

C. The loosening effect of the three atoms of bromine on the three nitro groups. This is a much weaker action than *B*, since with the tetrabrombenzol ‖ ($Br_4 1,2,4,6$) the atom of bromine (which stands in the

* These Proceedings, XXVII. 283.

† If the solvent was benzol and alcohol, less of the nitro groups were replaced; but this case need not be considered in this discussion.

‡ These Proceedings, XXXIII. 176.

§ Rec. Trav. Chim. Pays Bas, IX. 208.

‖ Jackson and Calvert, These Proceedings, XXXI. 132.

same position toward the three atoms of bromine as the three nitro groups do in our body) was removed only after long boiling of the benzol and alcohol solution, and then incompletely.

D. The loosening effect of the three bromine atoms on each other. This is a feeble effect, as Blau * found it necessary to heat symmetrical tribrombenzol to 120°–130° with sodic ethylate to obtain much effect. Calvert and one of us † found that with sodic ethylate a reaction took place at the boiling point of alcohol in open vessels, but the reaction ran more slowly, and was less complete than that with tetrabrombenzol.

We have then the most powerful loosening effect *A*, and the weakest loosening effect *D*, exerted on the atoms of bromine, while the two intermediate effects *B* and *C* influence the nitro groups, so that $A + D$ is very nearly, if not quite, equal to $B + C$; that is, the attack of the sodic ethylate will be directed about equally upon the atoms of bromine and upon the nitro groups, which was the result of our experimental work as stated above.

A similar discussion of the action of sodic ethylate on tribromdinitrobenzol gives the following results. The loosening effects are marked by letters, and arranged in order of intensity, as before.

E. The action of the two nitro groups in loosening the three atoms of bromine. This is a strong effect, as shown by the ease with which the bromdinitrobenzol $Br1(NO_2)_2 2,4$, is decomposed by potassic hydrate.‡

F. The effect of the three atoms of bromine on the two nitro groups already discussed.

G. The effect of the three atoms of bromine on one another, which has also been considered in the previous discussion.

H. The effect of the two nitro groups on each other. So far as we can find, this effect is too feeble to produce a replacement of a nitro group by an ethoxy group, but it should not be left out of account, as Lobry de Bruyn § has found that potassic cyanide in alcoholic solution converts metadinitrobenzol into $C_6H_3NO_2OC_2H_5CN$, which shows a certain loosening of one of the nitro groups.

Here then we have only one strong loosening agency (*E*), and this acts on the atoms of bromine, while of the other three by far the feeblest (*H*) is one of those acting on the nitro groups. It is evident therefore that

$$E + G > F + H,$$

* Monatsh. f. Chem., VII. 630.   ‡ Clemm, Journ. Pr. Chem., [2], I. 145.
† These Proceedings, XXXI. 134.   § Rec. Trav. Chim. Pays Bas, II. 205.

or, putting it into words, the attack upon the nitro groups will be insignificant compared to that on the atoms of bromine. This is in accord with our experimental results already given, since the attack on the nitro groups (Reaction III.) was to the attack on the atoms of bromine (Reactions I. and II.) as 1 to 66.

From the yields of the two bromdinitroresorcine diethylethers, given earlier in this paper, it is possible to draw conclusions in regard to the effect of the position of the nitro groups in loosening the atoms of bromine, but there is some question whether such conclusions are valid, since the difference between the yields of the two bromdinitroresorcine diethylethers is only ten per cent, and this amount is within the probable limit of error in this case, where the purifications were made by crystallization. On the other hand, the product melting at 92° (2) was obtained in the larger quantity, and this is the one where we should expect the greatest loss, since in its purification the crystallizations were the most numerous. We feel, therefore, justified in giving the following discussion with all necessary reserve. In the two reactions (I. and II.) one of the atoms of bromine replaced occupied in each case the same position (orthopara) toward the nitro groups, and therefore the difference between the reactions depends on the position of the second atom of bromine replaced. In Reaction I. this atom of bromine was ortho to one nitro group and para to the other, and this reaction gave 28 per cent of the product compared to 38 per cent from Reaction II., in which the atom of bromine was in the ortho position to both nitro groups. It would seem, therefore, that the diortho position of the nitro groups exerted a stronger loosening effect upon the bromine than the orthopara position.

When the reaction between tribromdinitrobenzol and sodic ethylate is carried on at 70°, the products isolated by us were the dinitroresorcine diethylether melting at 133°, a little of the bromdinitroresorcine diethylether melting at 184°, and much of the isomeric substance melting at 92°. These were the only products we have succeeded in identifying, although we obtained indications of the presence of the tribromnitrophenol. There was also a crystalline substance melting at 112°, but in too small quantity for identification, and a great deal of tarry matter. The absence of the dinitrophloroglucine triethylether is surprising; we should account for it by supposing that the reaction ran for so short a time (ten minutes) that the bromdinitroresorcine melting at 92° did not undergo decomposition. The hypothesis that the phloroglucine ether formed was converted into tarry substances by the hot sodic ethylate seems to us less probable. The approximate yields of the two products of the reaction at 70° were: —

Dinitroresorcine diethylether, melting point 133° . . 16 per cent.
Bromdinitroresorcine diethylether, melting point 92°   9 per cent.

Total . . . . . .   25 per cent.

So that in this case 75 per cent of the substance was unaccounted for. Most of this undoubtedly went into the tarry products.

The most striking phenomenon in the action of sodic ethylate on tribromdinitrobenzol at high temperatures is the replacement by hydrogen of the atom of bromine in the otho position to both nitro groups. The fact that this reaction only takes place to a very limited extent in the cold may perhaps be accounted for by the sparing solubility of the bromdinitroresorcine diethylether melting at 184° in the cold alcohol and benzol, so that most of it is precipitated, and therefore removed from the action of the ethylate. On the other hand, as this ether is easily soluble in these liquids, when hot, it would be brought into the sphere of the reaction under these conditions, and the dinitroresorcine diethylether would be formed. The bromdinitroresorcine diethylether melting at 92° is soluble in the cold solvents, and this probably accounts for the fact that a considerable amount of it was converted into the dinitrophloroglucine triethylether even in the cold.

It is perhaps worth while to call attention to the fact that in the reactions described in this paper the action is confined either to the atoms of bromine or to the nitro groups; that is, if it has started in one set of radicals in the meta position to each other, it does not extend to the other set of radicals in the meta position to each other and ortho or para to the first set. This observation has been made frequently in the course of the investigation of which this is a part, and the principle has sometimes given valuable aid in interpreting experimental results. In only a single case has such an extension of the reaction beyond the limits of the first set of trimeta positions been observed; this was in the action of hot sodic ethylate on tribromtrinitrobenzol,* which gave first tribromnitroresorcine diethylether, and by further action bromnitroresorcine diethylether
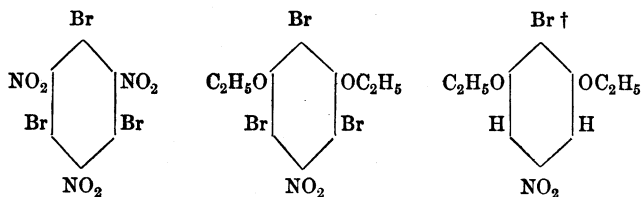
* These Proceedings, XXVII. 315.

† The position of the atom of bromine in this substance has not been established experimentally.

We are not, however, inclined to be too sure of the general occurrence of this restriction of reactions to a single trimeta zone, since the exceptional action just mentioned, in which the second trimeta zone was invaded, was accompanied by the formation of much tarry matter, and therefore it is possible that the tarry products so frequent in these reactions may have been formed by similar invasions of the second trimeta zone. The bearing of these observations on the benzol formula of J. N. Collie * is obvious.

Preparation of Symmetrical Tribromdinitrobenzol.

The description of the preparation of tribromdinitrobenzol is scattered through a number of papers from this Laboratory, so that it would be a matter of some difficulty to find it, and there would be danger that anyone looking it up might not find the latest and best form of the process ; we have thought it well, therefore, to give here a connected account of this process.

To make tribromaniline, 60 grams of aniline were treated with dilute hydrochloric acid, and dissolved in four litres of water. Then a rapid stream of air saturated with bromine vapor was drawn through the liquid by means of a Bunsen pump, until it assumed a distinct yellow color, which did not change for several minutes. The amount of bromine required was about 320 grams. The precipitate of tribromaniline was filtered out through cheese-cloth, washed until free from acid, and dried by pressing with a screw press, followed by heating to about 60° over a steam radiator.

To convert this tribromaniline into tribrombenzol, 100 grams of it were dissolved in 600 c.c. of alcohol and 150 c.c. of benzol by the aid of heat; 40 c.c. of common strong sulphuric acid were then added to the hot solution from a pipette, and any precipitate formed was dissolved by longer heating, or even adding more of the solvents. Forty grams of finely powdered sodic nitrite were next sifted into the hot solution as rapidly as the violence of the reaction permitted, and the product heated, until there was no more effervescence, after which it was allowed to stand at ordinary temperatures over night, and then filtered and dried.

The tribrombenzol was converted into tribromdinitrobenzol as follows. The perfectly dry tribrombenzol was mixed with four or five times its weight of fuming nitric acid of specific gravity 1.51, and gently heated over a low flame for two hours in a flask closed with a porcelain

* 2 Proc. Chem. Soc., 1896–1897, p. 143.

crucible, taking care that the temperature was kept just below boiling. It was then allowed to stand over night at ordinary temperatures, when most of the tribromdinitrobenzol crystallized out, while the rest of it was obtained by pouring the supernatant acid liquid into a large excess of water. The dried product was purified by crystallization from about eight times its weight of a mixture of three parts of alcohol with one of benzol.

Action of Sodic Ethylate on Tribromdinitrobenzol at 70°.

The tribromdinitrobenzol used in all this work, made in the way described in the previous section, melted at 192°, and had the constitution $Br_3 1,3,5,(NO_2)_2 2,4$. Forty grams of this tribromdinitrobenzol were dissolved in 80 c.c. of benzol, and mixed with the solution of sodic ethylate obtained from 6.8 grams of sodium and 180 c.c. of absolute alcohol, which gave the proportion of three molecules of sodic ethylate to each molecule of tribromdinitrobenzol. The flask containing the mixture was then placed in a water bath, which was heated until a thermometer immersed in the mixture rose to 70°, at which temperature the solution was kept for ten minutes. The liquid turned dark brown during this heating, a color which had been found to be characteristic of the reaction with the aid of heat. At the end of the ten minutes the liquid was poured into a large evaporating dish, and the solvents allowed to evaporate spontaneously. The residue thus obtained was washed with water until the wash waters became colorless, and the products purified as follows.

Residue Insoluble in Water.

This residue was dried and extracted three times with boiling ligroin. The portion insoluble in ligroin was purified by repeated crystallization from a mixture of ligroin and benzol, during which it was frequently treated with boneblack. The product was the dinitroresorcine diethyl-ether already obtained in this way by W. H. Warren and one of us; * it was recognized by its melting point, 133°, and its solubilities and appearance.

The ligroin solution on standing deposited a flocculent precipitate in too small quantity for identification, which was filtered out, and the filtrate evaporated to dryness; the crystalline residue was spread on an unglazed plate to remove oily impurities, after which it was purified by crystallization from hot ligroin. After four crystallizations it showed

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* These Proceedings, XXV. 170.

the constant melting point 92°, when it was dried *in vacuo*, and analyzed with the following results : —

I. 0.2043 gram of the substance gave by the method of Carius 0.1136 gram of argentic bromide.

II. 0.2885 gram of the substance gave 20.6 c.c. of nitrogen at a temperature of 12° and a pressure of 745 mm.

	Calculated for $C_6HBr(OC_2H_5)_2(NO_2)_2$.	Found. I.	II.
Bromine	23.89	23.69	
Nitrogen	8.36		8.32

The substance is therefore a bromdinitroresorcine diethylether isomeric with the one obtained by W. H. Warren and one of us [*] by the action of cold sodic ethylate upon the tribromdinitrobenzol and melting at 184°. As the constitution of this substance has been established (in this paper) as $OC_2H_51,OC_2H_55,Br3,NO_22,NO_24$, it follows that our new bromdinitroresorcine diethylether must have the constitution

$$OC_2H_51,OC_2H_53,Br5,NO_22,NO_24,$$
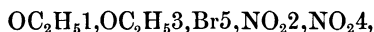
as this is the only other body with this composition which can be obtained from this tribromdinitrobenzol.

Properties of Bromdinitroresorcine Diethylether.   Melting Point 92°.
$$C_6HBr(OC_2H_5)_2(NO_2)_2.   (OC_2H_5)_21,3,Br5,(NO_2)_22,4.$$
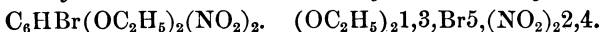
This substance crystallizes in white needles thickly crowded into bunches shaped like hour-glasses; when better developed, they form prisms with blunt ends, which seem to be made up of a basal plane modified by very minute planes of a pyramid.   On long exposure to the air, especially in bright light, it turns brownish, and this change is accompanied by decomposition.   It melts at 92°; and is freely soluble even in the cold in benzol, ether, chloroform, acetone, glacial acetic acid, carbonic disulphide, or acetic ester; somewhat soluble in cold alcohol, freely in hot; sparingly soluble in cold ligroin, freely in hot; essentially insoluble in water whether cold or hot.   Ligroin is the best solvent for it.   A hot solution of sodic hydrate has little or no action on it.   On heating it with sodic ethylate it is converted almost quantitatively into the triethylether of dinitrophloroglucine formed by the replacement of its atom of bromine by an ethoxy group; the product was recognized by its melting point 105°, and its other properties.   The wash waters

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* These Proceedings, XXV. 166.

gave no test for a nitrite, showing that the nitro groups had not been attacked.

Other Products of the Reaction. — During the purification of the dini-troresorcine diethylether a small quantity of the bromdinitroresorcine diethylether melting at 184° was isolated. Its presence shows that the heating for ten minutes used by us was not sufficient to convert the whole of it into the dinitroresorcine diethylether.

From the ligroin mother liquors of the bromdinitroresorcine diethylether melting at 92°, a few milligrams of a body were obtained, which melted constant at 112°, contained bromine, and gave no test for nitrogen after fusion with sodium.* We supposed, therefore, that we had the tribromresorcine, which melts according to Benedikt at 111°, and could be formed by the replacement of the two nitro groups by ethoxy radicals, followed by saponification ; but upon comparing our specimen with some tribromresorcine made for this purpose, it was found that, although the two substances melted at the same point, (as we found the melting point 112°–113° for the tribromresorcine,) they differed markedly in solubility in alcohol, our substance being much the less soluble, and also in the method of crystallization, although the forms were not incompatible. That our substance was not tribromresorcine was proved by the action of sodic hydrate, which did not affect our body, whereas it dissolved the tribromresorcine instantly, giving a solution which turned black almost at once. The amount of our substance was not enough for analysis, so we can make no statement in regard to its nature. We add a description of its crystalline form, which may lead to its identification. It forms when crystallized from alcohol white very sharp needles, which when better developed appear as slender prisms with square ends or bluntly sharpened by several planes at very obtuse angles to the sides and terminated by a basal plane. When less well developed, it forms felted masses of needles or bunches, or long sheaves of needles. None of the arborescent forms were observed which seemed to be characteristic of the tribromresorcine. This substance was also characterized by its solubility in ligroin. It was only formed in very minute quantities under the conditions of the reaction used by us.

The Products of the Reaction soluble in Water.

The wash waters obtained from the product of the action of sodic ethylate on tribromdinitrobenzol at 70° were highly colored, but the

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* We do not feel that this proves the substance is free from nitrogen.

substances obtained by acidifying them with acetic acid were so tarry that we could not isolate any body fit for analysis. The filtrate from this tar, which was also colored, was evaporated to small bulk, and treated with baric chloride, when a gelatinous precipitate was obtained, which resembled the barium salt of tribromnitrophenol described later in this paper. We did not however succeed in getting enough of it to purify for analysis.

The approximate yields of the principal products of the action of sodic ethylate on tribromdinitrobenzol at 70° were determined as follows: —

Dinitroresorcine Diethylether . . . . 16 per cent.
Bromdinitroresorcine Diethylether melting at 92° .   9 per cent.

Total . . . . 25 per cent.

From which it appears that 75 per cent of the theoretical yield had been converted into the tarry mass, from which we could isolate nothing fit for analysis.

Action of Sodic Ethylate upon Tribromdinitrobenzol in the Cold.

The proportions used were the same as those used in the experiment at 70°, that is, 40 grams of the tribromdinitrobenzol dissolved in 80 c.c. of benzol and mixed with the sodic ethylate from 6.8 grams of sodium and 180 c.c. of absolute alcohol. The mixture was allowed to stand in a corked flask from three to five days with frequent shaking, after which it was poured into an evaporating dish, and allowed to evaporate spontaneously. The residue was washed with water, until the washings were colorless, and the products were then purified as follows.

Residue Insoluble in Water.

This was dried, and extracted three times with boiling ligroin, which left a crystalline residue, and this after recrystallization from a mixture of alcohol and benzol showed the constant melting point 184°, and was therefore the bromdinitroresorcine diethylether discovered by W. H. Warren and one of us in the previous work on this reaction.

The ligroin extract was allowed to stand over night, when it deposited crystals, which were filtered out, and strangely enough proved to be essentially insoluble in ligroin. As they could not have been formed in the ligroin solution, we can explain the extraction of them by hot ligroin only by supposing they are soluble in a mixture of ligroin and the other (soluble) product of the reaction. The crystals after purification

by crystallization from a mixture of alcohol and benzol showed the constant melting point 105°, which suggested that they were the dinitrophloroglucine triethylether discovered by W. R. Lamar and one of us.* To settle the nature of the substance, it was dried at 100° and analyzed with the following result : —

0.2297 gram of the substance gave 19.4 c.c. of nitrogen at a temperature of 23° and a pressure of 750 mm.

	Calculated for $C_6H(OC_2H_5)_3(NO_2)_2$.	Found.
Nitrogen	9.34	9.42

It is therefore the dinitrophloroglucine triethylether.

The ligroin mother liquor, from which the dinitrophloroglucine triethylether had been deposited, was evaporated to dryness, and spread on a porous plate to remove oily impurities, after which it was dissolved in hot ligroin, and allowed to crystallize, when in addition to the square prisms of dinitrophloroglucine triethylether long needles with square ends were observed, which resembled the bromdinitroresorcine diethylether melting at 92°, obtained by the action of a hot sodic ethylate solution on tribromdinitrobenzol, as described earlier in this paper. The isolation of this substance from the mixture of crystals proved a matter of great difficulty. Hot ligroin did not accomplish this, and a number of other solvents were tried with no better success. Finally, on soaking the mixture for some time with cold ligroin, it was found that a considerable amount of the square prisms remained undissolved ; these were filtered out, and the filtrate on evaporation gave a residue, which was once more extracted with cold ligroin in the same way. This second extract yielded crystals, which could be purified by crystallization from hot ligroin, when their constant melting point 92° and their solubilities and crystalline form proved that they were the bromdinitroresorcine diethylether $(OC_2H_5)_2 1,3, Br5, (NO_2)_2 2,4$.

Although the dinitrophloroglucine triethylether was formed freely in the cold, we obtained none of it when we carried on the reaction at 70°. This was probably due to the short duration of our experiments (ten minutes), as there is little doubt that this substance is produced by the further action of the sodic ethylate on the bromdinitroresorcine diethylether at first formed. It follows that the best way of making the diethylether melting at 92° is the process described under the action of sodic ethylate at 70°.

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* Am. Chem. Journ., XVIII. 670.

Products of the Reaction Soluble in Water.

The first step in purifying the products of the reaction of sodic ethyl-ate on tribromdinitrobenzol in the cold consisted in washing with water; the highly colored wash waters were concentrated, and acidified with acetic acid, which produced a flocculent precipitate; this was dissolved in dilute alcohol, filtered, and the hot filtrate treated with an aqueous solution of baric hydrate. On cooling, beautiful leaf-like lemon-yellow crystals of a barium salt separated, which, after purification by recrystal-lizing from water, were dried at 100°, and the barium determined with the following result : —

0.3916 gram of the salt gave 0.1446 gram of baric sulphate.

	Calculated for $[C_6H_2(OC_2H_5)(NO_2)_2O]_2Ba2H_2O$.	Found.
Barium	21.78	21.71

The retention of the two molecules of water at 100° is certainly strange, especially as the salt changed from lemon-yellow to orange on heating, evidently from loss of water, and, as therefore this analysis was not suf-ficient to establish the identity of the substance, we prepared the free phenol by decomposing the barium salt with acetic acid. It was recrys-tallized from alcohol, until it showed the constant melting point 77°, when it was dried *in vacuo*, and analyzed with the following result : —

0.2125 gram of the substance gave 22.1 c.c. of nitrogen at a tempera-ture of 15° and a pressure of 752 mm.

	Calculated for $C_6H_2OHOC_2H_5(NO_2)_2$.	Found.
Nitrogen	12.28	12.11

The body is therefore a dinitroresorcine monoethylether, and seems to be identical with that discovered by Aronheim[*] by treating nitrosoresor-cine ethylether with nitric acid, as the descriptions of the appearance and solubilities of the two bodies coincide, but Aronheim gives the melt-ing point 75°, whereas we found 77°. It seemed necessary therefore to establish the identity of our body more firmly, and this was done by saponifying a specimen of it by boiling for half an hour with a sulphuric acid of specific gravity 1.44. As the dinitroresorcine thus obtained melted at 212° our body has the symmetrical structure

$$OH1.OC_2H_5 5.NO_2 2.NO_2 4,$$

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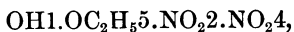
[*] Ber. d. chem. Ges., XII. 32.

and is the monoethylether corresponding to the diethylether formed by the action of hot sodic ethylate on tribromdinitrobenzol (see later in this paper). Whether our substance is identical with that discovered by Aronheim, or whether the difference of two degrees in the melting point is caused by a difference in constitution, we are unable to determine with our present knowledge.

The filtrate, from which the dinitroresorcine monoethylether had been precipitated by acetic acid, still contained a phenol to judge by its color, and to obtain this hydrochloric acid was added, which produced a white precipitate. Without filtering the liquid was extracted with ether, and, as this removed almost all of the color, the aqueous liquid was thrown away. The ether on evaporation usually left a red oily mass, which obstinately refused to crystallize; on one occasion, however, we succeeded in obtaining about half a gram of a solid, which after recrystallization from alcohol showed the constant melting point 90°, and agreed in its properties with those described for the tribromnitrophenol which melts at 89° according to Daccomo.* To characterize the substance more thoroughly some of the oily mass was treated with a solution of baric hydrate, and the barium salt formed, which had a gelatinous consistency, was washed with cold water, dissolved in cold alcohol, from which it was allowed to crystallize, and after being dried at 100° analyzed with the following result : —

0.1816 gram of the salt gave 0.0485 gram of baric sulphate.

	Calculated for $(C_6HBr_3NO_2O)_2Ba$.	Found.
Barium	15.45	15.70

There can be no doubt, therefore, that the phenol is tribromnitrophenol formed from tribromdinitrobenzol by the replacement of one of the nitro groups by one hydroxyl radical. Our substance also shows two characteristic properties, which have been observed in the case of the tribromnitrophenol; these are the solubility of its barium salt in alcohol, and the fact that the sodium salt is not decomposed by organic acids. The constitution of the phenol follows from its mode of formation from tribromdinitrobenzol melting at 192°. It is $Br_3 1,3,5, OH 2. NO_2 4$.

The following statement of the yields of these various products of the action of cold sodic ethylate on tribromdinitrobenzol will give a general idea of the extent to which each of the reactions takes place, but it should be remembered that these numbers are approximate estimates

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* Ber. d. chem. Ges., XVIII. 1167.

rather than strict determinations, as must necessarily be the case where the products are purified by crystallization. The numbers are percentages of the theoretical yield in each case : —

$C_6HBr(OC_2H_5)_2(NO_2)_2$, melting point 184° . . 22 per cent.
$C_6HBr(OC_2H_5)_2(NO_2)_2$, melting point 92° . . 19 per cent.
$C_6H(OC_2H_5)_3(NO_2)_2$, melting point 105° . . 19 per cent.
$C_6H_2(OC_2H_5)OH(NO_2)_2$, melting point 77° . . 6 per cent.
$C_6HBr_3(NO_2)OH$, melting point 90° . . . . 1 per cent.

Total . . . . . . 67 per cent.

It appears from this that the principal reaction is that which forms the bromdinitroresorcine diethylether melting at 92°, since the dinitrophloroglucine triethylether must be formed from this by a secondary reaction, and the yield of the two together is 38 per cent. Next after this comes the reaction forming the bromdinitroresorcine diethylether melting at 184°, and its decomposition product, the dinitroresorcine monoethylether, as these together make up 28 per cent of the theoretical yield; while the third primary reaction, that which forms the tribromnitrophenol, is of very inferior importance, yielding only one per cent. These results also make it probable that no other product was formed in any considerable amount, as the percentage unaccounted for (33) is no greater than the loss which would be expected from such numbers of crystallizations, and other wasteful methods of purification, as were necessary in isolating the substances enumerated. Small quantities of oily products were observed at various points in the work, as stated in the description of the purification, but except for these all the products were recognized.

Constitution of the Dinitroresorcine Diethylether melting at 133°.

The dinitroresorcine diethylether was boiled for some time with sulphuric acid of specific gravity 1.44 in a flask with a return cooler. The reaction runs smoothly, and gives an almost quantitative yield of the symmetrical dinitroresorcine $(OC_2H_5)_2 1,5,(NO_2)_2 2,4$. This was recognized by its melting point 210°–211°; Typke [*] gives 212°.5, Schiaparelli and Abelli [†] 214°.5, both of which are higher than that observed by us; but, as only two dinitroresorcines could be formed from tribromdinitrobenzol, the symmetrical one, whose melting point is given above, and the adjacent, which melts at 142°, there can be no doubt about the iden-

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[*] Ber. d. chem. Ges., XVI. 552.
[†] Ibid., XVI. 872.

tity of our substance. Many of its other properties also coincided with those given for symmetrical dinitroresorcine. It formed vitreous yellowish prisms apparently belonging to the monoclinic system when crystallized from acetic ester, but crystallized from alcohol in the spear-head forms, which were obtained by Typke from sublimation. The sodium salt was orange-red, the ammonium salt yellow prisms, the silver salt a red precipitate which soon turned brown. The acid barium salt consisted of rather thick yellow needles. We did not succeed in getting the carmine red neutral barium salt. The free phenol decomposes carbonates.